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Phosphoric Acid - Catalyzed Hydrolysis of Benzeneboronic Acid

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PHOSPHORIC ACID - CATALYZED HYDROLYSIS OF BENZENEBORONIC ACID

by

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TABLE OF CONTENTS

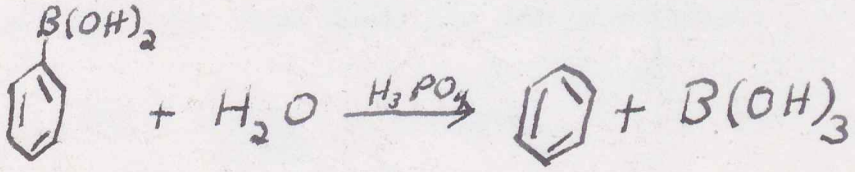
INTRODUCTION

The kinetics of the protodeboranation of benzeneboronic acid have been studied using strong acid catalysts. First - order rate plots have been obtained with aqueous sulfuric, phosphoric, and perchloric acids at various acid concentrations and temperatures. (1) (2) (3)

The original workers found one exception. At a phosphoric acid concentration of over 80%, the kinetics are not first - order, but instead, the reaction appears to be autocatalytic (4). It is the purpose of this research to determine if this phenomenon is real, and if so, to elucidate the cause of the autocatalysis. To do this, conditions at which the first - order kinetics are observed will be studied to standardize procedures. When reproducible results have been obtained, then one can proceed to investigate for the autocatalysis.

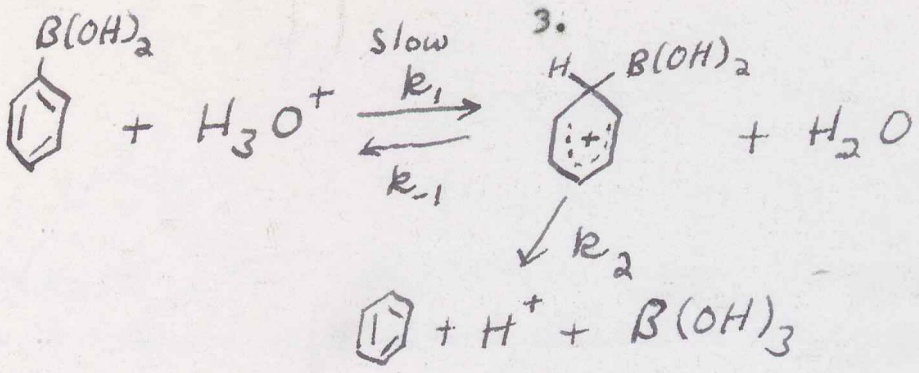
HISTORICAL

The aromatic boronic acids represent a group of compounds whose hydrolysis only recently have received very much attention. This research is concerned with one particular areneboronic acid, namely benzeneboronic acid, and its hydrolysis in aqueous phosphoric acid solutions.



This acid-catalyzed reaction is important for two reasons. First, if the mechanism could be established, it might yield a better understanding of the kinetic characteristics of acid catalysis in strongly acid media. Secondly, since this reaction is that of an electrophilic attack by a proton, it presents a test of the applicability of linear free energy relations to this type of reaction.

Kuivila and Nahabedian have shown the mechanism of the acid-catalyzed hydrolysis to involve a proton transfer from acid to substrate as the rate-determining step (1) (2) (3).



For the hydrolysis of benzeneboronic acid, all of the rate experiments performed showed first-order kinetics; that is, the rate data fit the equation,

$$\log C = \frac{-kt}{2.303} + \text{constant} \qquad \text{(I)}$$

where k is the pseudo-first order rate coefficient and C is the concentration of benzeneboronic acid at time t.

This is derived from the basic first-order rate equation:

$$\frac{dC}{dt} = -kC \qquad \text{(II)}$$

which upon integration yields equation (I).

The one exception to this data, is a deviation from first-order kinetics at an acid strength of over 80% H_3PO_4. Instead of the usual first-order plot, the reaction rate increases, that is, becomes autocatalytic. No other acid studied but phosphoric, showed this phenomenon.

EXPERIMENTAL

Reagents - A sample of benzeneboronic acid was obtained from Professor Nahabedian. This was recrystallized and converted to the anhydride whose melting point could be easily reproduced. Dehydration was accomplished by drying in an oven at 110° C. The samples used melted at 216° (uncor.). All other reagents were the purest grade available commercially and were used without further purification.

Kinetic Methods - Kinetic solutions were prepared by diluting appropriate amounts of aqueous acid and aqueous boronic acid stock solutions to a desired volume. The initial concentration of boronic acid stock solution was approximately 10^{-2}M. This solution was then added to acid to make the kinetic solution. This solution was 10^{-3}M. The kinetic solutions were placed in a thermostated bath whose temperature varied no more than 0.05° C. At appropriate intervals 10 ml. aliquots were removed by pipet, and the reaction quenched by dilution with 90 ml. of water and cooling, simultaneously.

The concentration of unreacted boronic acid was determined spectrophotometrically using a Beckman DU spectrophotometer. At 218 mμ the absorptivity of benzeneboronic acid is 8450, whereas that for benzene is 55. A residual absorbance of .085 due to the phosphoric acid was found. This residual absorbance was found at concentrations of 78-81% H_3PO_4. This absorbance is dependent on the acid concentration, but in the range investigated, the change in absorbance is negligible. Thus the concentration of unreacted substrate C, is given by log C = log(absorbance - .085) +log constant. This relation results from the fact that the absorptivity of benzene at 218 mμ is negligibly small.

The per cent of phosphoric acid used was obtained by titration with .9540 M NaOH using bromphenol blue as the indicator. A 5 ml. sample of the acid was pipeted and diluted to 50 ml. Ten milliliters of the diluted solution was then titrated. By this method the grams per liter of H_3PO_4 was determined which could then be converted to per cent acid.

EXPERIMENTAL RESULTS

A total of twelve runs were made. These ranged from 67% acid at 30°C to 81% acid at 40°C. Since some of the results are duplicated, four different ones will be presented in this paper. Each of the following tables is plotted and found at the end of the report, Table 1 corresponding to Graph 1, etc. It follows from the first-order rate equation that a plot of log absorbance vs. time will yield a slope equal to $\frac{k}{2.303}$, where k is the pseudo first-order rate constant. As would be expected, a ten degree change in temperature caused the rate-constant to change by a factor of two to three. A ten per cent change in the phosphoric acid concentration, affected the rate constant by a power of ten.

Table 1

Temperature - 30.1°C 66.9% H_3PO_4

time (hours)	Absorbance
4.5	.755
18.0	.487
24.0	.464
42.5	.265
48.0	.215
65.5	.149
71.0	.140
90.5	.110
96.0	.106

Table 2

Temperature - 30.1°C 66.9% H_3PO_4

$k = 1.05 \times 10^{-5}$ sec^{-1}

time (hours)	(Absorbance - .085)
4.5	.670
18.0	.402
24.0	.379
42.5	.180
48.0	.130
65.5	.064
71.0	.055
90.5	.025
96.0	.021

Table 3

Temperature - 39.8°C 68.5% H_3PO_4

$k = 2.20 \times 10^{-5}$ sec^{-1}

time (hours)	(Absorbance - .085)
.25	.785
2.75	.651
4.75	.565
6.25	.510
7.75	.426
10.75	.345
12.25	.310
24.75	.108
28.50	.095

Table 4

Temperature - 39.8°C 77.7% H_3PO_4

$k = 4.17 \times 10^{-4}$ sec^{-1}

time (min.)	(Absorbance - .085)
15	.660
30	.518
45	.390
60	.313
75	.235
105	.153
135	.090
165	.053
195	.035

Table 5

Temperature - 40.0°C 81.1% H_3PO_4

time (min.)	(Absorbance - .085)
10	1.40
15	1.15
20	1.00
25	.840
30	.715
35	.610
40	.500
50	.330
60	.210

SUMMARY

The results are expected, but still not explainable. For most of the year, the first-order plots could not be reproduced. The reason for this was the tacit assumption that the absorbance at infinite time was zero. After months of frustration, this was found to be decidedly not the case. A residual absorbance due to the phosphoric acid was detected. Since the original workers found no evidence for this residual absorbance, this discovery was a complete surprise. An example of results before and after the residual absorbance correction was introduced are shown in Graphs 1 and 2. After this correction was made, first order plots were always obtained.

The results appear to concur with those of the original workers. Above an acid concentration of 80%, the autocatalysis begins to be observed. Instead of the usual straight line, a plot showing two slopes is obtained. (See Graph 5) During the course of the reaction, the initial slope shows a 20 per cent increase. Logically, there is no immediate explanation for the phenomenon. Unfortunately, the entire year was spent just

trying to determine of the phenomenon were real. Now that this has been acheived, it remains for someone else to explain the cause of it.

Since the cause of the difficulty of this researcher has been determined to be the residual absorbance, the next researcher will not have to spend valuable time trying to get first-order plots. After developing the technique involved with kinetic studies, the researcher should proceed to add substituents to the benzene ring and determine the rate constants at high acid concentrations. Will substituted boronic acids show autocatalysis above 80% phosphoric acid? What is the cause for the autocatalysis? These questions remain to be answered.

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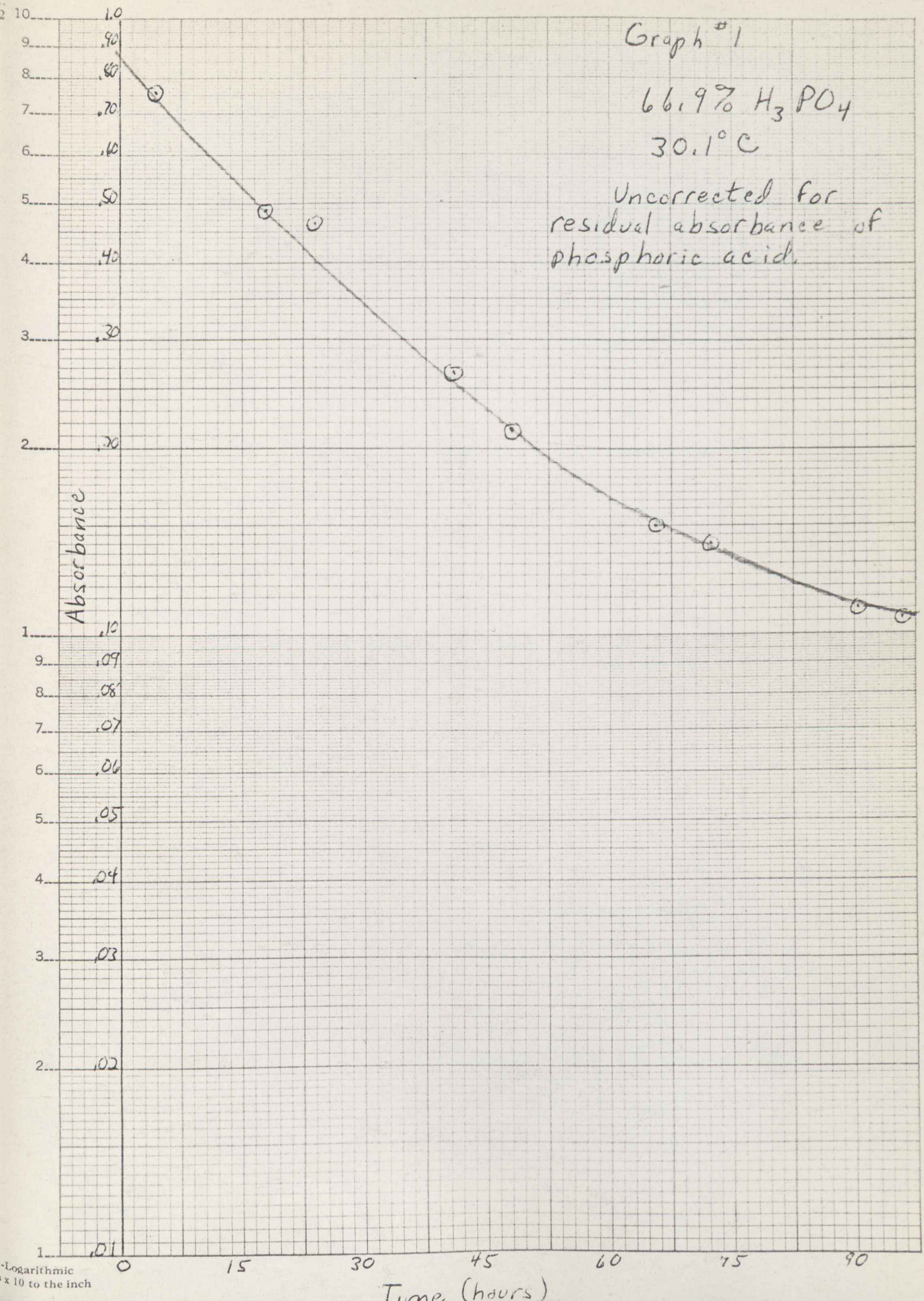
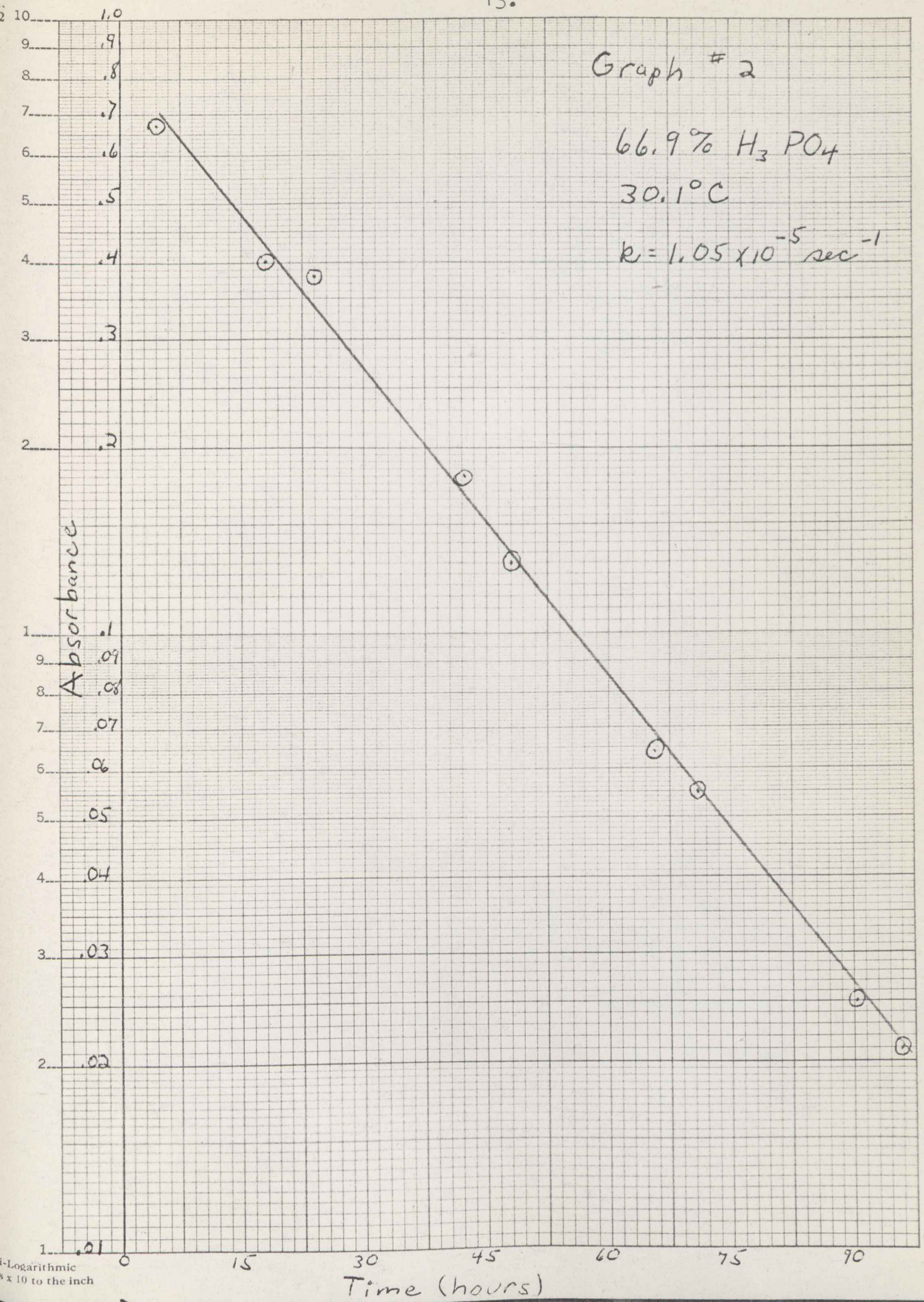
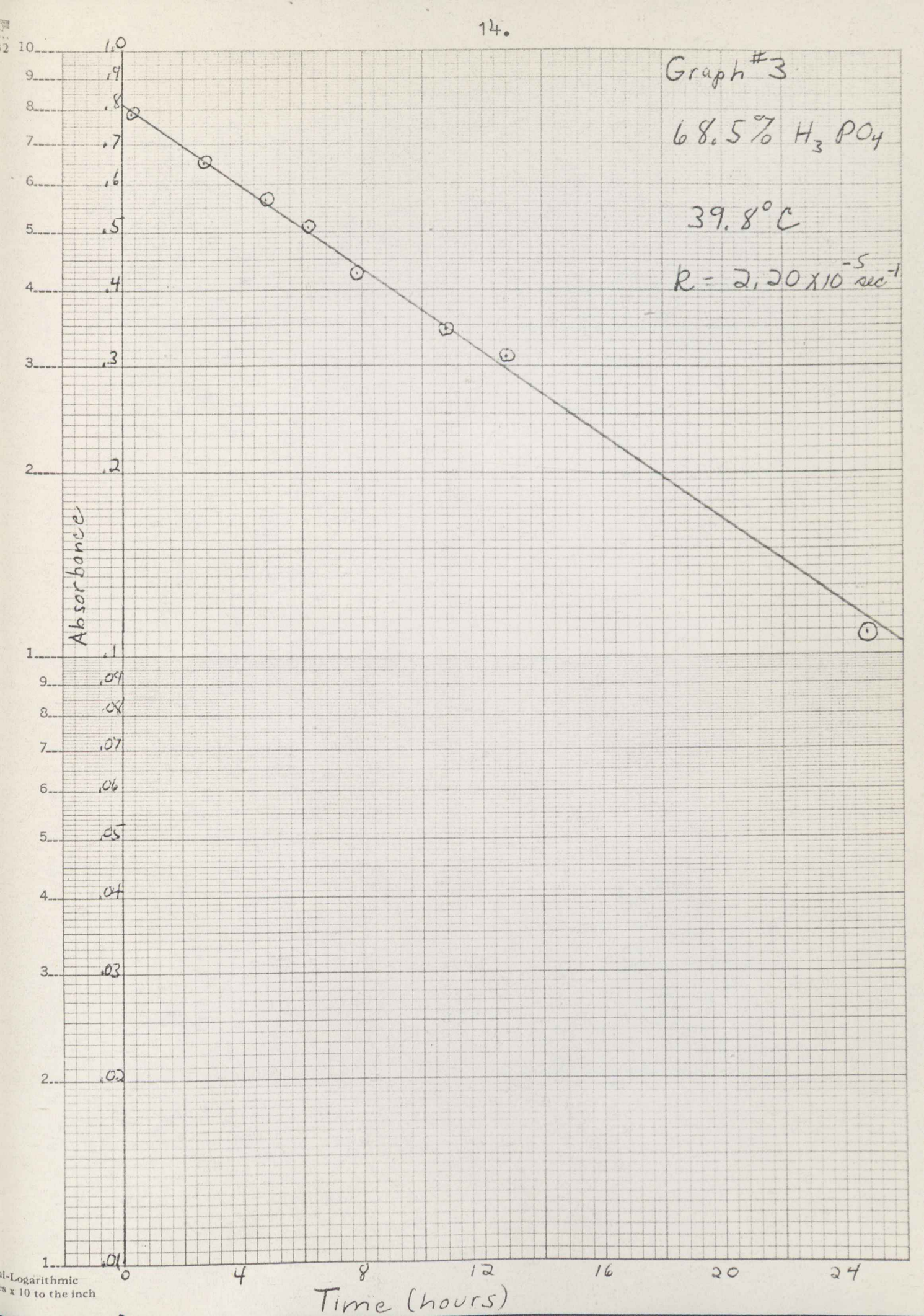


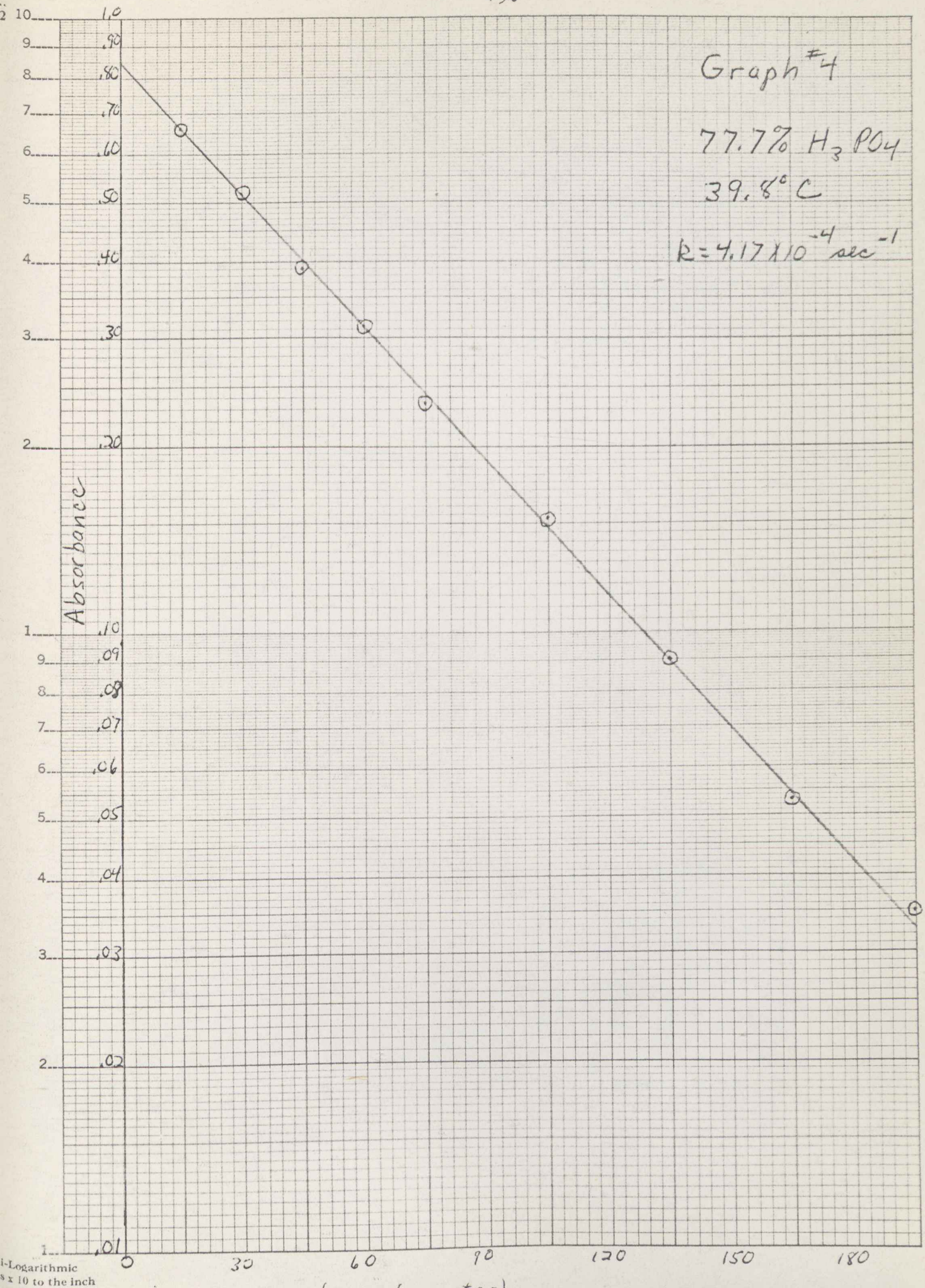
-Logarithmic
x 10 to the inch



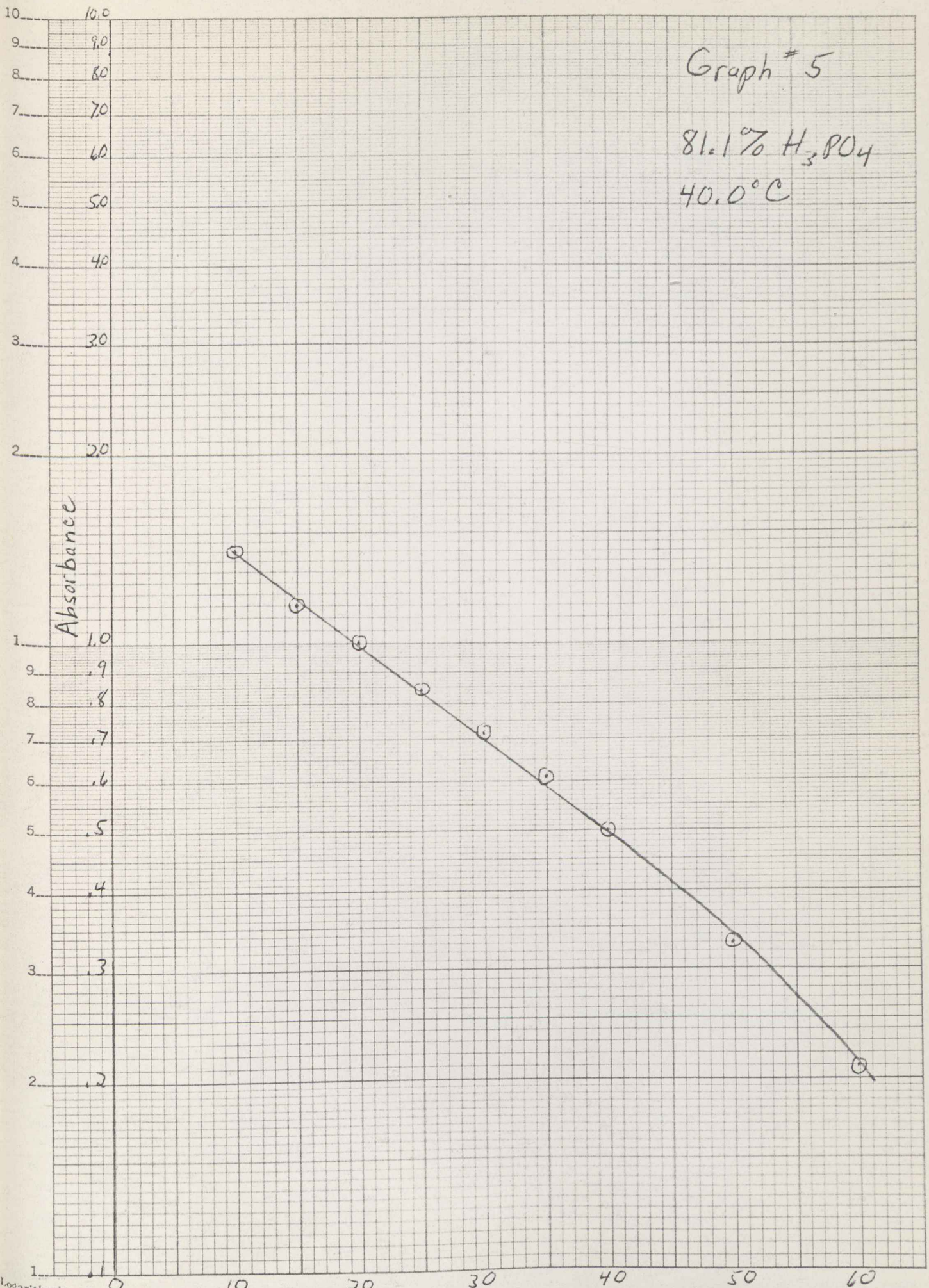
Semi-Logarithmic
8 x 10 to the inch



Semi-Logarithmic
Cycles x 10 to the inch



Semi-Logarithmic
5 x 10 to the inch


Graph # 5
81.1% H_3PO_4
40.0°C
Absorbance
time (minutes)
0
10
20
30
40
50
60
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
Logarithmic
x 10 to the inch